Neutron scattering studies of the magnetic order in RNi_2B_2C

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Neutron diffraction has been used to investigate the magnetic order of RNi_2B_2C. For R=Er the system orders antiferromagnetically at $T_N=6.8$ K, and this long range order coexists with superconductivity ($T_c=11$ K). The magnetic structure is an incommensurate, transversely polarized spin-density-wave state, with the modulation wave vector δ along the a axis and the moments along b. δ has a temperature-independent value of 0.5526 $(2\pi/a)$, with the structure squaring up at low temperatures. For R=Ho the moments also prefer to reside in the $a-b$ plane, but initially an incommensurate c-axis spiral state forms upon cooling, with $T_N \approx T_C \approx 8$ K. This c-axis spiral consists of ferromagnetic sheets of holmium moments in the $a-b$ plane, but with each sheet rotated by $\sim 163°$ as one proceeds along the c axis. Small a-axis peaks are also observed above the reentrant superconducting transition over a narrow temperature range, but the c-axis peaks dominate. Just below the reentrant transition at ~ 5 K the magnetic system locks-in to a simple commensurate antiferromagnetic structure, which permits superconductivity to be restored. The c-axis spiral, the a-axis component, the commensurate antiferromagnetic structure, and the superconducting phase are all in a delicate balance energetically, and this balance may be easily shifted by subtle changes in composition, magnetic field, and pressure. $DyNi_2B_2C$ orders antiferromagnetically at $T_N=11$ K, with the same commensurate antiferromagnetic structure as found for the holmium material at low temperature. The existence of superconductivity in some samples of $DyNi_2B_2C$ is consistent with the antiferromagnetic structure observed.
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I. INTRODUCTION

The interaction between magnetic long range order and superconductivity has been an active area of interest for many years. In the Chevrel-phase and related compounds[1] the magnetic ordering temperatures are typically much lower than the superconducting transitions, and are in the temperature range where dipolar interactions play a crucial role. An even more extreme situation is found for the high-T_c cuprate superconductors, where the rare earth ordering is typically ~ 1 K while the superconducting transitions are one to two orders of magnitude higher in temperature.[2] The new classes of quaternary intermetallic borocarbide superconductors such as the RNi_2B_2C (R=magnetic rare earth ion) materials[3] have therefore attracted considerable attention because the magnetic ordering of the rare earth ions typically occurs at a much higher temperature,[4–12] which requires that exchange interactions dominant the energetics rather than dipolar interactions. The T_c's are also comparable to the magnetic transition temperatures so that the interplay between these two cooperative phenomena is enhanced. Moreover, the evidence to date suggests that the superconductivity is three-dimensional in nature, unlike the layered cuprates, and that it originates from a relatively strong electron–phonon interaction so that the theories advanced to explain the original systems can be more readily compared and tested experimentally in these new materials. We have therefore been carrying out neutron scattering experiments to explore the nature of the magnetism and its interaction with superconductivity.[4–8]

The samples were prepared by melting the elements Y, Er, Ho, Dy, or Ce (purity 99.9%), Ni (99.9%), B (99.8%), and C (99.7%) in an arc-furnace under a protective atmosphere of flowing argon. The ^{11}B isotope was used to reduce the effects of nuclear absorption in the samples. The powder diffraction measurements were carried out on the diffractometers at National Institute of Standards and Technology (NIST), and more recently at the high-flux-isotope reactor (HFIR) spectrometers at the Oak Ridge National Laboratory when the NIST facilities were unavailable. A standard top-loading pumped He cryostat with a low T capability of 1.7 K was employed to control the sample temperature. Data were collected on samples of Er, Ho, Dy, Ce, and Y. No magnetic order was found in either the $Y^{(6)}$ or Ce systems, and so no further discussion of these materials will be given here.

II. RESULTS AND DISCUSSION

A. $HoNi_2B_2C$

The first system to be investigated with neutrons was $HoNi_2B_2C$ because of the doubly reentrant superconducting behavior exhibited by this material.[3] Both the magnetic order and the superconductivity begin to develop at ~ 8 K, and

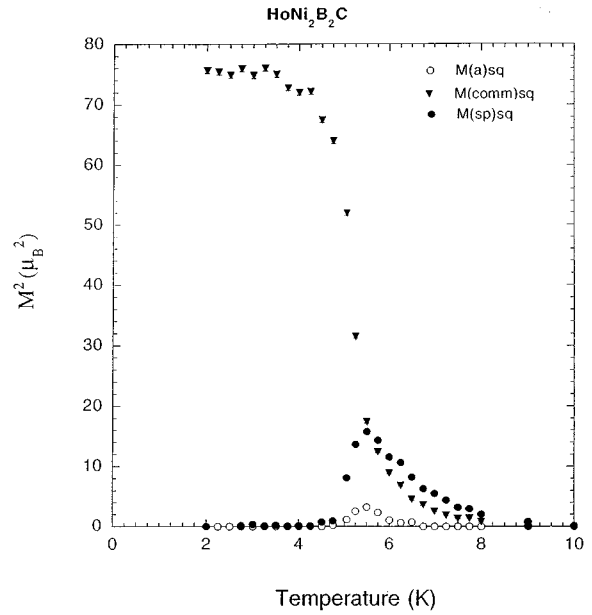

FIG. 1. Temperature dependence of the commensurate antiferromagnetic (▼) Bragg peaks, the incommensurate c-axis spiral peaks (●), and incommensurate the a-axis magnetic peaks (○) for this sample of $HoNi_2B_2C$. These data were taken on cooling.

initially two types of magnetic peaks were observed.[4] One set of peaks originates from a long-wavelength c-axis spiral antiferromagnetic structure, where the moments in the tetragonal plane are ferromagnetically aligned, but they spiral along the c axis with a relative alignment of 163°. Thus this magnetic periodicity is incommensurate with the underlying chemical unit cell. The second set of peaks originates from a commensurate magnetic structure in which the Ho moments are again ferromagnetically aligned within the tetragonal plane, but are antiferromagnetically coupled along the c axis (i.e., a relative alignment of 180°). The temperature evolution of these two types of peaks is shown in Fig. 1, where the intensities have been normalized to the nuclear peaks. Upon cooling through the ordering temperature we see that the intensity of the spiral peak in this sample is about twice the intensity of the (001) commensurate antiferromagnetic peak, which is quite different than found for other samples.[4,5,7–9] Thus the relative ratio of these two types of peaks varies dramatically from sample to sample, and demonstrates that these two types of magnetic order occur in distinct regions of the sample. Indeed, it is now clear[12] that both the magnetic and superconducting states are very sensitive functions of the sample composition for all these materials.

Upon further cooling the antiferromagnetic intensity begins to rapidly increase, while the intensity of the spiral state drops rapidly. This is just the temperature regime where the reentrant superconductivity is observed; the superconducting state that initially forms on cooling is quenched, but then is regained at lower temperature as the spiral intensity disappears and the antiferromagnetic state becomes fully established. At low T only the commensurate antiferromagnetic order survives in this sample, and this magnetic order readily coexists with the superconductivity. Hence we believe that the spiral magnetic order and superconductivity are strongly coupled and competing states, with the development of the spiral amplitude driving the system normal.[4,5,7,8,13] The simple commensurate antiferromagnetic state, on the other hand, is not strongly coupled to the superconductivity, which allows the coexistence at low temperature.

Finally, we note that there is also a small component of the magnetism associated with an incommensurate a-axis modulation found by Goldman *et al.*,[9] as also shown in Fig. 1. The intensity of this peak is much smaller than for the spiral peaks, and exists over a narrower temperature range. In particular, note that the development of the c axis and antiferromagnetic intensities occur together, and they start at a higher temperature where the a-axis intensity is zero. We also note that the maximum in intensity for the a-axis and c-axis reflections occurs at about the same temperature for this particular sample, while for other samples they occur at quite different temperatures. The relative intensity of these a-axis peaks and the temperature range where they appear also vary substantially from sample to sample. These results suggest that these a-axis peaks again originate from separate regions of the sample, and emphasizes that the antiferromagnetic, c-axis spiral, a-axis, and superconducting states are all delicate functions of the sample composition.

B. $DyNi_2B_2C$

The Dy ions in $DyNi_2B_2C$ order antiferromagnetically at a T_N just above 10 K. Within the $a-b$ plane the moments are ferromagnetically aligned, while the structure is antiferromagnetic along the c axis.[10] This is the same commensurate, collinear antiferromagnetic structure that is found in the $HoNi_2B_2C$ material at low temperature. The superconducting state is very sensitive to the precise composition of the sample, and is present in some samples while absent in others.[14,15] If the superconducting state is present then there appears to be little interaction between it and the magnetic order parameter, with the two coexisting to low temperatures as found for $HoNi_2B_2C$.

The intensity of the (001) antiferromagnetic Bragg peak is shown in Fig. 2 as a function of temperature. The intensity varies smoothly with temperature, with no evidence of any hysteresis (in contrast to the case of $HoNi_2B_2C$). The solid curve is a fit to the $S=1/2$, $2d$ Ising model, with the fit being restricted to the data below 9 K to avoid the effects of critical scattering. The overall fit is relatively good, with $T_N=10.16$ K. However, this curve should be regarded primarily as a ''guide-to-the-eye'' rather than as establishing the $2d$ Ising model as appropriate; a more definitive test could be made with an extinction-free single crystal. We also tried fitting the data to a mean field model with a variable spin, but the fitted curve was not steep enough and the fit was not nearly as good. Finally, we obtained a low temperature ordered moment of 8.47(9) μ_B from the profile refinements of the full diffraction pattern.

C. $ErNi_2B_2C$

For the Er system the superconducting transition occurs at $T_c \approx 11$ K, and superconductivity persists to low temperatures with no reentrant transitions or evidence of strong cou-

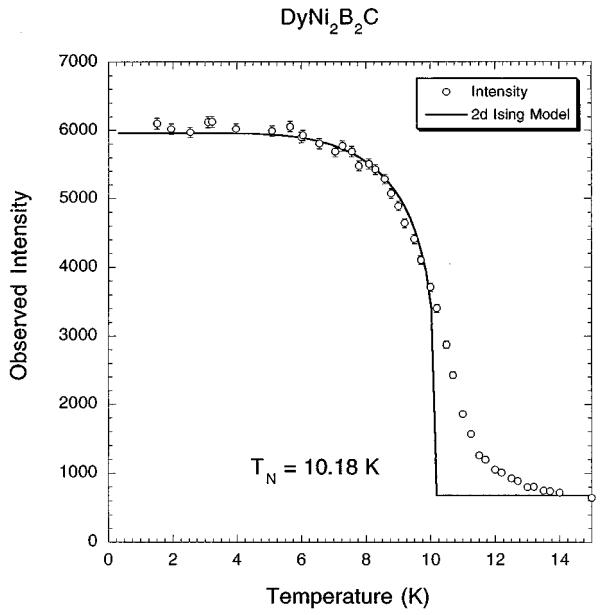

FIG. 2. Temperature dependence of the intensity of the (001) magnetic reflection for $DyNi_2B_2C$. The solid curve is a fit to the $2d$ Ising model.

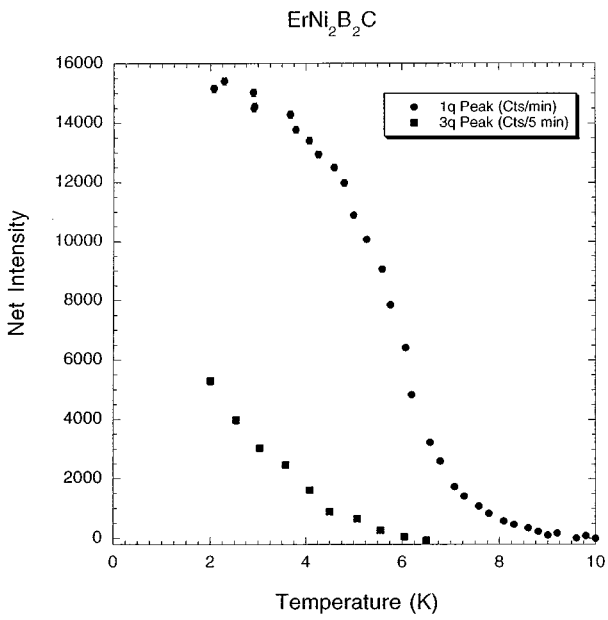

FIG. 3. Temperature dependence of the primary spin density wave intensity, and the third harmonic, in $ErNi_2B_2C$.

pling to the magnetic state. The antiferromagnetic ordering develops at T_N=6.8 K,[6,11] with the Er ions forming a transversely polarized, incommensurate spin density wave state. The modulation wave vector for this state is δ=0.5526 ($2\pi/a$) and is approximately temperature independent, with the direction along the a axis (or equivalently along the b axis in this tetragonal system) with the spins directed along b (or a). The staggered magnetization increases smoothly as the temperature is decreased below T_N as shown in Fig. 3, and is nonhysteretic. Higher-order harmonics of δ also develop at lower temperatures, as also shown in Fig. 3, and indicate a squaring-up of the magnetic structure as we go to low T. This squaring-up of the spin density wave is expected, since a purely sinusoidal spin density wave cannot be the ground state of a local-moment system because this leaves many of the moments in a partially disordered state.

A refinement of the magnetic structure gives an ordered moment of 7.8 μ_B/Er ion. There is also evidence of an induced moment of -0.35 μ_B on the Ni ions, as the refinement gives a small improvement when a Ni moment is included. However, such a small Ni moment is difficult to resolve unambiguously from the large Er moment, and it might indicate that a small adjustment in the model is needed rather than an actual Ni moment. In particular, from a physical standpoint an ordered Ni moment is difficult to reconcile with the coexistent superconducting state since it is believed that the Ni electrons are the ones that are predominantly involved in the Cooper pairing. The spin-depairing would then be expected to suppress the superconductivity if indeed the superconducting state originates from conventional BCS-type electron–phonon pairing. Clearly additional work will be needed to clarify this issue.

We note that the magnetic structure observed in $ErNi_2B_2C$ is reminiscent of the small a-axis peaks found in the $HoNi_2B_2C$ material as discussed above. Since this large-moment magnetic structure readily coexists with superconductivity in the Er system, it seems unlikely that the weak a-axis peaks in the Ho material could be the cause of the reentrant behavior in $HoNi_2B_2C$. Thus this is additional evidence that the reentrant superconducting behavior in the holmium system is associated with the incommensurate c-axis magnetic ordering.

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